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Establishment of Uncertainty Ranges and Probability Distributions of Actinide Solubilities for Performance Assessment in the Waste Isolation Pilot Plant (WIPP)

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OUTLINE OF PRESENTATION

- Introduction
- Fracture Matrix Transport (FMT) Code
- Waste Isolation Pilot Plant (WIPP)
- Thermodynamic Model
- Experimental Data
- Cumulative Distribution Functions of Am(III), Th(IV) and Np(V) Models
- Conclusions

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INTRODUCTION

- Accurate prediction of actinide solubilities in various solutions is important to the performance assessment (PA) of geological repositories for nuclear waste.
- Some repositories are in salt formations, and therefore associated brines are of high ionic strength in nature.
- Activity coefficient models employed in common geochemical codes: Davies equation ($I \leq 0.1$ m); B dot equation ($I \leq 1.0$ m); Pitzer equation (from very dilute solutions to solutions with high ionic strengths)
- Some codes have the Pitzer model, but do not have databases with actinides.

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FRACTURE MATRIX TRANSPORT (FMT) CODE

- **FMT code developed at Sandia National Laboratories (Babb and Novak, 1997 and addenda) featuring:**
  - **Pitzer equations for calculation of activity coefficients of aqueous species**
  - **Actinide complexes with organic ligands expected in WIPP (acetate, citrate, EDTA, and oxalate)**
  - **Actinide oxidation state analog model: Nd(III), Am(III) and Cm(III) are used to predict actinide solubilities in +III state; Th(IV) is employed to predict actinide solubilities in +IV state; Np(V) is utilized to predict actinide solubilities in +V state.**
  - **Qualified for predicting solubilities of actinides for the Waste Isolation Pilot Plant (WIPP)**

Babb S.C., and Novak C.F., (1997), and addenda. User's Manual for FMT Version 2.3: A Computer Code Employing the Pitzer Activity Coefficient Formalism for Calculating Thermodynamic Equilibrium in Geochemical Systems to High Electrolyte Concentrations. Albuquerque, NM: Sandia National Laboratories. ERMS 243037.

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THE WASTE ISOLATION PILOT PLANT (WIPP)

- **The WIPP is a U.S. Department of Energy geological repository being used for the permanent disposal of defense-related transuranic waste, located about 40 km east of Carlsbad, southeastern New Mexico, U.S.A.**

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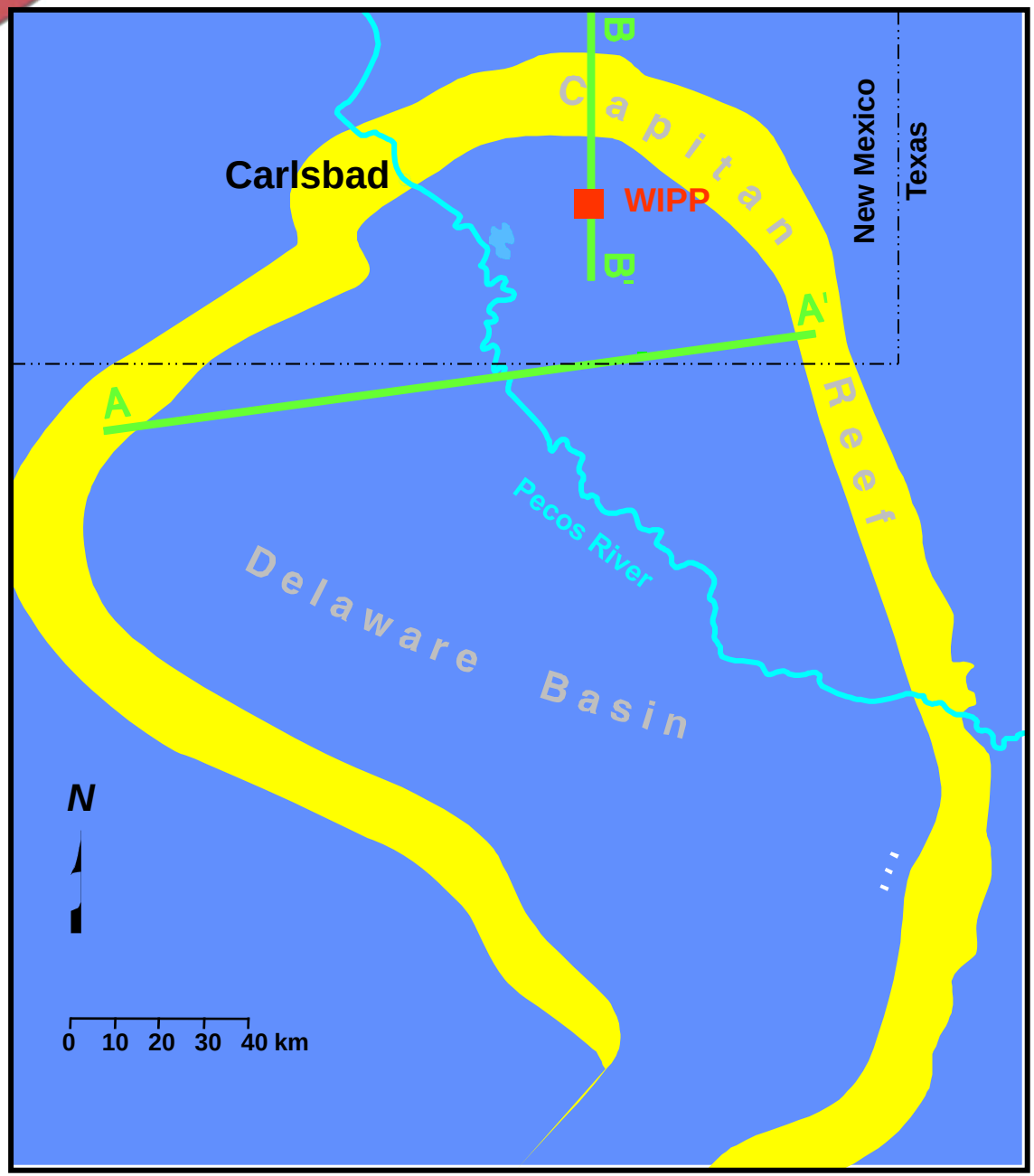

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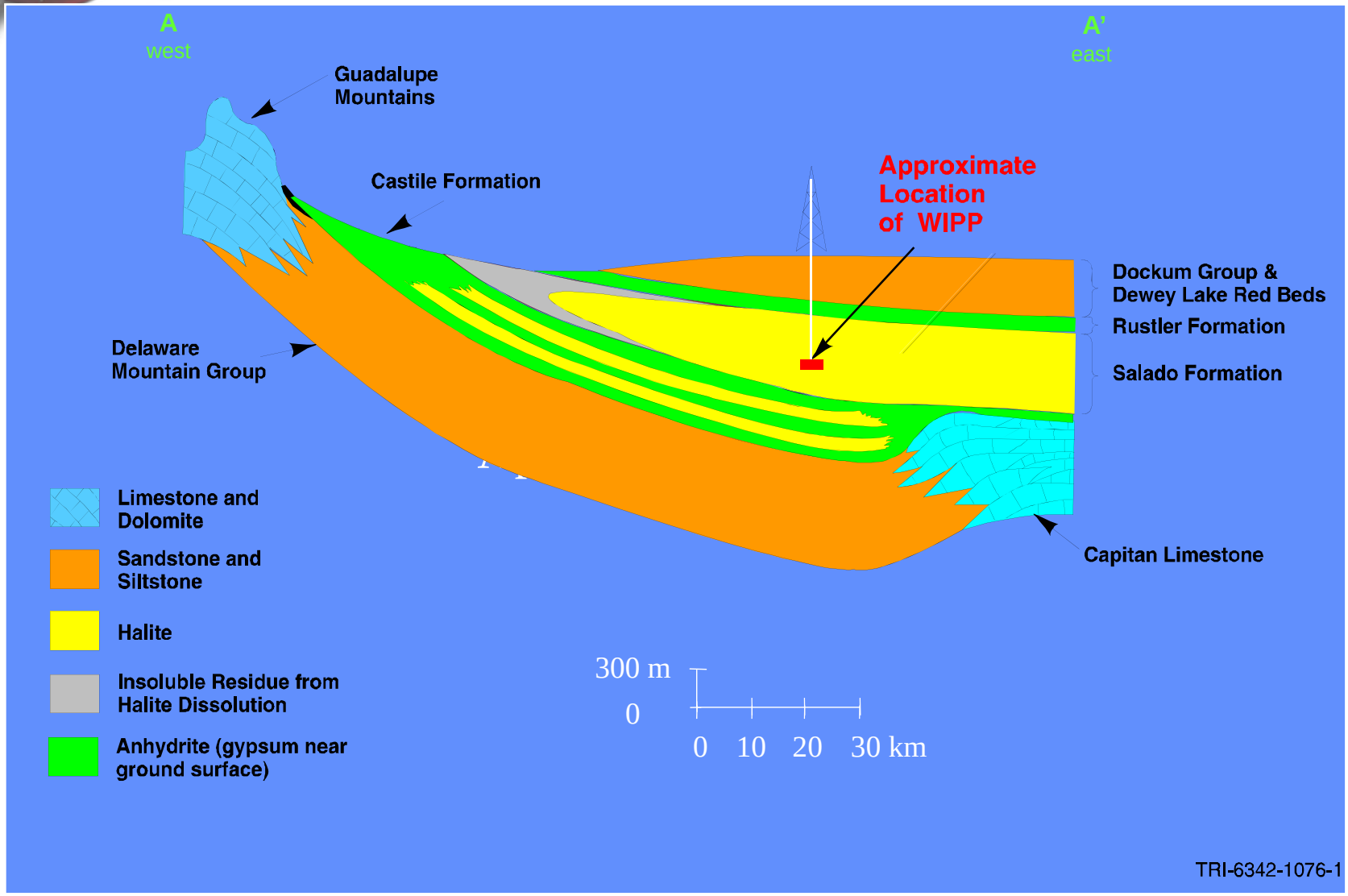

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THERMODYNAMIC MODEL: AM(III) MODEL

Aqueous and solid species and their Gibbs free energies of formation at reference state (298.15 K and 1 bar) of Am(III) model in the FMT code

Species	$\Delta_f G$, kJ mol^{-1}
Am^{3+}	-599.116
$AmCO_3^+$	-1,173.200
$Am(CO_3)_2^-$	-1,729.026
$Am(CO_3)_3^{3-}$	-2,269.433
$Am(CO_3)_4^{5-}$	-2,784.705
$AmOH^{2+}$	-793.123
$Am(OH)_2^+$	-983.819
$Am(OH)_3^o$	-1,163.880
$AmCl^{2+}$	-731.747
$AmCl_2^+$	-857.424
$AmSO_4^+$	-2,109.450
$Am(SO_4)_2^-$	-1,362.260
$AmAc^{2+}$	-980.016
$AmCit^o$	-566.517
$AmEDTA^-$	-575.889
$AmOx^+$	-601.989
$AmOHCO_3$(cr)	-1,413.770
$Am(OH)_3$(s)	-1,227.809
$NaAm(CO_3)_2 \cdot 6H_2O$ (cr)	-3,461.597

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THERMODYNAMIC MODEL: TH(IV) MODEL

Aqueous and solid species and their Gibbs free energies of formation at reference state (298.15 K and 1 bar) of Th(IV) model in the FMT code

Species	$\Delta_f G$, kJ mol^{-1}
Th^{4+}	-704.547
$Th(CO_3)_5^{-6}$	-3,498.551
$Th(OH)_3(CO_3)^-$	-1,922.639
$Th(OH)_4^o$	-1,553.192
$Th(SO_4)_2^o$	-2,259.915
$Th(SO_4)_3^{2-}$	-3,009.286
$ThAc^{3+}$	-1,111.812
$ThCit^+$	-708.689
$ThEDTA^o$	-707.502
$ThOx^{2+}$	-737.270
ThO_2 (am)	-1,118.959
$Th(SO_4)_2 \cdot 8H_2O$	-4,164.416
$Th(SO_4)_2 \cdot 9H_2O$	-4,402.135
$Th(SO_4)_2 \cdot Na_2SO_4 \cdot 6H_2O$ (289.15 K)	-4,985.624
$Th(SO_4)_2 \cdot K_2SO_4 \cdot 4H_2O$ (289.15 K)	-4,555.004
$Th(SO_4)_2 \cdot 2K_2SO_4 \cdot 2H_2O$ (289.15 K)	-5,408.312
$Th(SO_4)_2 \cdot 3.5K_2SO_4$ (289.15 K)	-6,917.963

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THERMODYNAMIC MODEL: NP(V) MODEL

Aqueous and solid species and their Gibbs free energies of formation at reference state (298.15 K and 1 bar) of Np(V) model in the FMT code

Species	$\Delta_f G$, kJ mol^{-1}
NpO_2^+	-914.945
$NpO_2CO_3^-$	-1,471.429
$NpO_2(CO_3)_2^{3-}$	-2,007.427
$NpO_2(CO_3)_3^{5-}$	-2,528.926
NpO_2OH^o	-1,087.532
$NpO_2(OH)_2^-$	-1,254.872
NpO_2Ac^o	-1,288.032
NpO_2Cit^{2-}	-852.087
$NpO_2H_2EDTA^-$	-902.533
NpO_2EDTA^{3-}	-832.159
NpO_2Ox^-	-906.878
NpO_2OH(am)	-1,126.299
NpO_2OH(aged)	-1,122.303
$NaNpO_2CO_3 \cdot 3.5H_2O$(s)	-1,048.058
$Na_3NpO_2(CO_3)_2$(s)	-2,837.249
$KNpO_2CO_3$(s)	-1,802.919
$K_3NpO_2(CO_3)_2$(s)	-2,909.008

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THERMODYNAMIC MODEL: PITZER INTERACTION PARAMETERS OF AM(III) MODEL

Pitzer interaction parameters involving Am(III) species

Binary interaction parameters				
Species *i*	Species *j*	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}
Am^{3+}	Cl^-	0.5856	5.6	-0.0166
Am^{3+}	SO_4^{2-}	1.792	15.04	0.600
$AmCO_3^+$	Cl^-	-0.072	0.403	0.0388
$AmOH^{2+}$	Cl^-	-0.055	1.6	0.05
$Am(OH)_2^+$	Cl^-	-0.616	-0.45	0.05
$AmCl^{2+}$	Cl^-	0.593	3.15	-0.006
$AmCl_2^+$	Cl^-	0.516	1.75	0.010
$AmSO_4^+$	Cl^-	-0.091	-0.39	0.048
$AmAc^{2+}$	Cl^-	0.3088	1.74	-0.132
$AmOx^+$	Cl^-	-0.9374	0.29	0.248
Na^+	$Am(CO_3)_2^-$	-0.240	0.224	0.0284
Na^+	$Am(CO_3)_3^{3-}$	0.125	4.73	0.0007
Na^+	$Am(CO_3)_4^{5-}$	2.022	19.22	-0.305
Na^+	$Am(SO_4)_2^-$	-0.345	0.40	0.051
Na^+	$AmEDTA^-$	-0.2239	0.29	0.095
Interaction parameters for neutral species and mixing parameters				
Species *i*	Species *j*	λ_{ij}	θ_{ij}	
$Am(OH)_3^o$	Na^+	-0.2		
$Am(OH)_3^o$	Cl^-	-0.2		
$AmCit^o$	Cl^-	-0.406		
Am^{3+}	Ca^{2+}		0.2	
$AmCl^{2+}$	Ca^{2+}		-0.014	
$AmCl_2^+$	Ca^{2+}		-0.196	
Am^{3+}	Na^+		0.1	

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THERMODYNAMIC MODEL: PITZER INTERACTION PARAMETERS OF TH(IV) MODEL

Pitzer interaction parameters involving Th(IV) species

Binary interaction parameters				
Species *i*	Species *j*	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}
Th^{4+}	Cl^-	1.092	13.7; $\beta^{(2)}$= -160	-0.112
Th^{4+}	SO_4^{2-}	1.56	0	0
Th^{4+}	HSO_4^-	1.44	0	0
$ThAc^{3+}$	Cl^-	1.061	5.22	0.109
$ThCit^+$	Cl^-	-0.7467	0.29	0.319
$ThOx^{2+}$	Cl^-	-0.343	1.74	0.5
Na^+	$Th(CO_3)_5^{-6}$	1.31	30	0
Na^+	$Th(SO_4)_3^{2-}$	0.12	0	0
K^+	$Th(SO_4)_3^{2-}$	0.90	0	0
Interaction parameters for neutral species and mixing parameters				
Species *i*	Species *j*	Species *k*	λ_{ij} or θ_{ij}	Ψ_{ijk}
$Th(SO_4)_2^o$	Cl^-		0.29	
$Th(SO_4)_2^o$	HSO_4^-		0.68	
$ThEDTA^o$	Cl^-		0.1111	
Th^{4+}	Na^+	Cl^-	0.42	0.21
Th^{4+}	Mg^{2+}	Cl^-	0.60	0.21
Th^{4+}	H^+	Cl^-	0.60	0.37
Na^+	$Th(CO_3)_5^{-6}$	Cl^-	2.0	-0.08

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THERMODYNAMIC MODEL: PITZER INTERACTION PARAMETERS OF NP(V) MODEL

Pitzer interaction parameters involving Np(V) species

Binary interaction parameters				
Species *i*	Species *j*	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}
NpO_2^+	Cl^-	0.1415	0.281	0
Na^+	$NpO_2CO_3^-$	0.1	0.34	0
Na^+	$NpO_2(CO_3)_2^{3-}$	0.48	4.4	0
Na^+	$NpO_2(CO_3)_3^{5-}$	1.80	22.7	0
Na^+	NpO_2Cit^{2-}	-0.4226	1.75	0.142
Na^+	$NpO_2H_2EDTA^-$	-0.8285	0.2575	0.256
Na^+	NpO_2EDTA^{3-}	0.683	5.911	0
Na^+	NpO_2Ox^-	-0.5418	0.29	0.095
K^+	$NpO_2(CO_3)_3^{5-}$	2.34	22.7; $\beta^{(2)}$= -96	-0.22
Mg^{2+}	$NpO_2CO_3^-$	0.1	0.34	0
Mg^{2+}	$NpO_2(CO_3)_2^{3-}$	0.48	4.4	0
Mg^{2+}	$NpO_2(CO_3)_3^{5-}$	2.07	22.7; $\beta^{(2)}$= -48	-0.11
Interaction parameters for neutral species and mixing parameters				
Species *i*	Species *j*	Species *k*	λ_{ij} or θ_{ij}	Ψ_{ijk}
NpO_2OH^o	Cl^-		-0.19	
$NpO_2CO_3^-$	Cl^-	Na^+	-0.21	0
$NpO_2(CO_3)_2^{3-}$	Cl^-	Na^+	-0.26	0
$NpO_2(CO_3)_3^{5-}$	Cl^-	Na^+	-0.26	0
$NpO_2(CO_3)_3^{5-}$	CO_3^{2-}	K^+	-1.9	0

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Establishment of Uncertainty Ranges and Probability Distribution of Actinide Solubilities

- **Experimentally measured solubilities of actinides which were not used in model development are compared with predicted values.**
- ***D* value, i.e., difference between measured and predicted values, is defined as**

$$D = \log_{10} S_m - \log_{10} S_p$$

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EXPERIMENTAL DATA

- **Experimental data are from various supporting solutions:**
  - **Simple Solutions: NaCl, $NaHCO_3$, Na_2CO_3, $NaClO_4$, KCl, K_2CO_3, etc., Ionic strength up to 14.9 M**
  - **Binary Mixtures: NaCl+$NaHCO_3$, NaCl+Na_2CO_3, KCl+K_2CO_3, etc., Ionic strength up to 8.1 M**
  - **Ternary Mixtures: NaCl+Na_2CO_3+KCl, $NaHCO_3$+Na_2CO_3+$NaClO_4$, etc., Ionic strength up to 7.1 M**
  - **Multi-component synthetic brines relevant to WIPP: AISinR brine, I = 0.84 M; H-17, I = 2.8 M; ERDA-6, I = 5.6 M; SPC, I = 7.1 M; G Seep, I = 7.3 M; Brine A, I~7.8 M**

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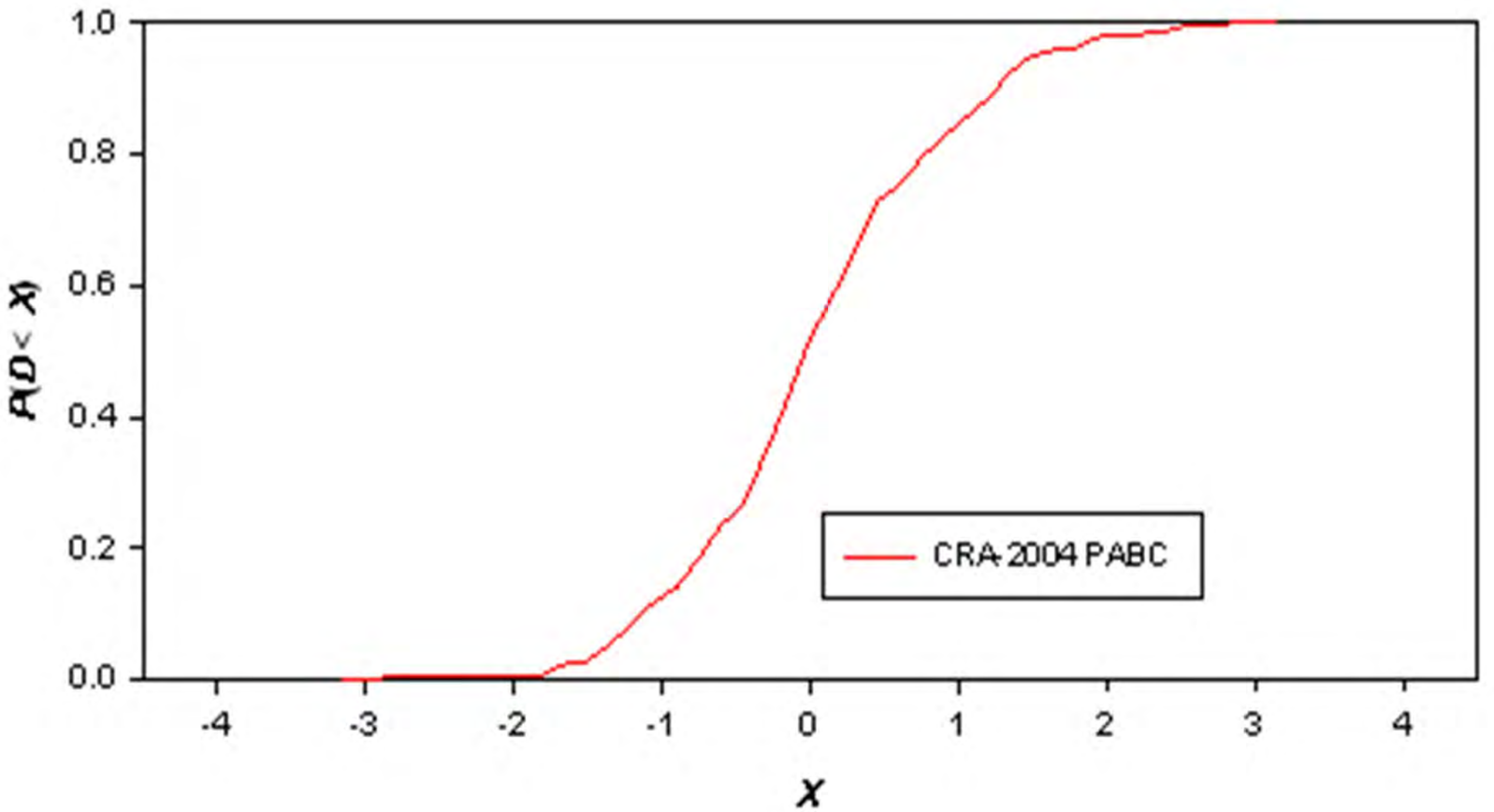
CUMULATIVE DISTRIBUTION FUNCTION FOR AM(III)



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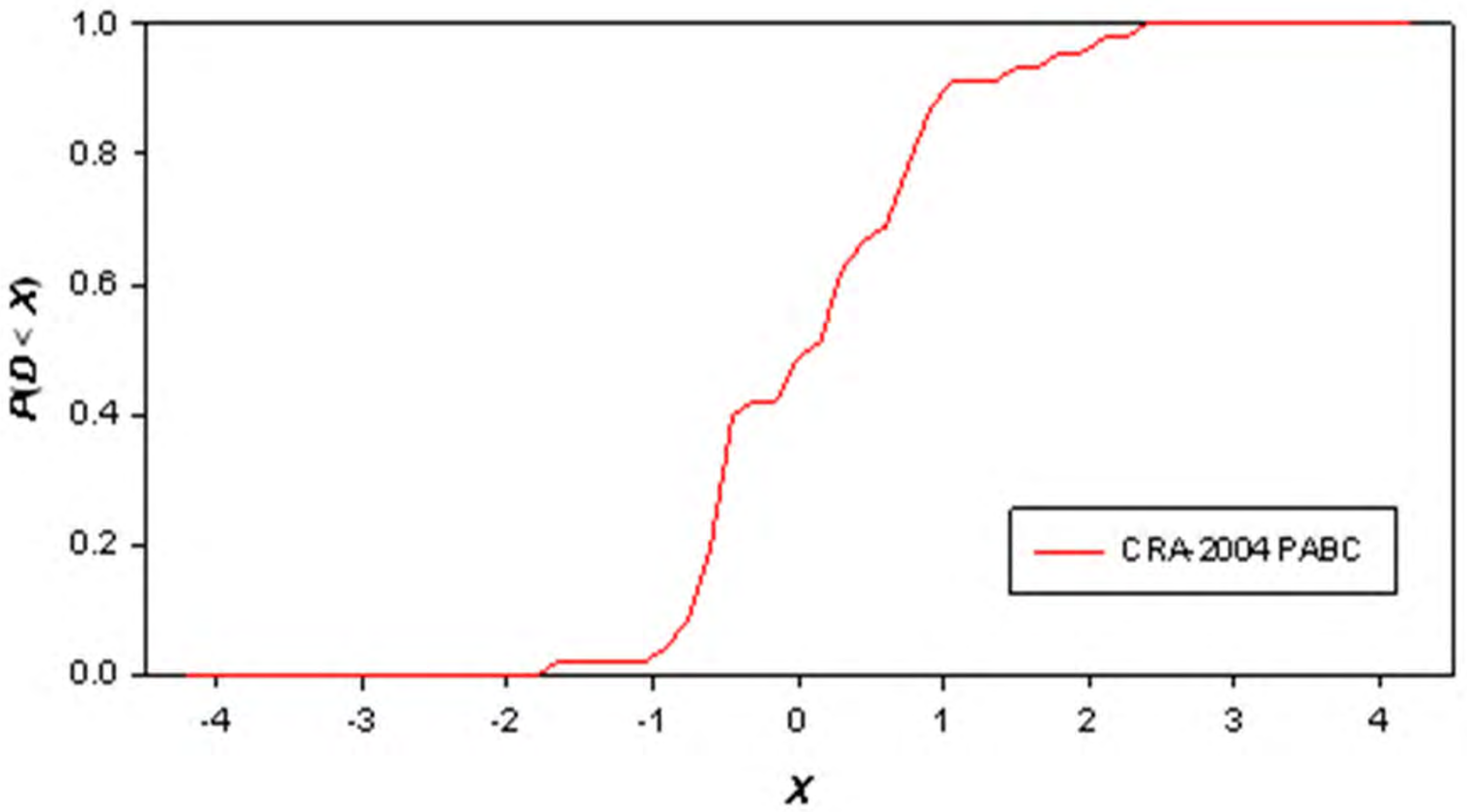
CUMULATIVE DISTRIBUTION FUNCTION FOR TH(IV)



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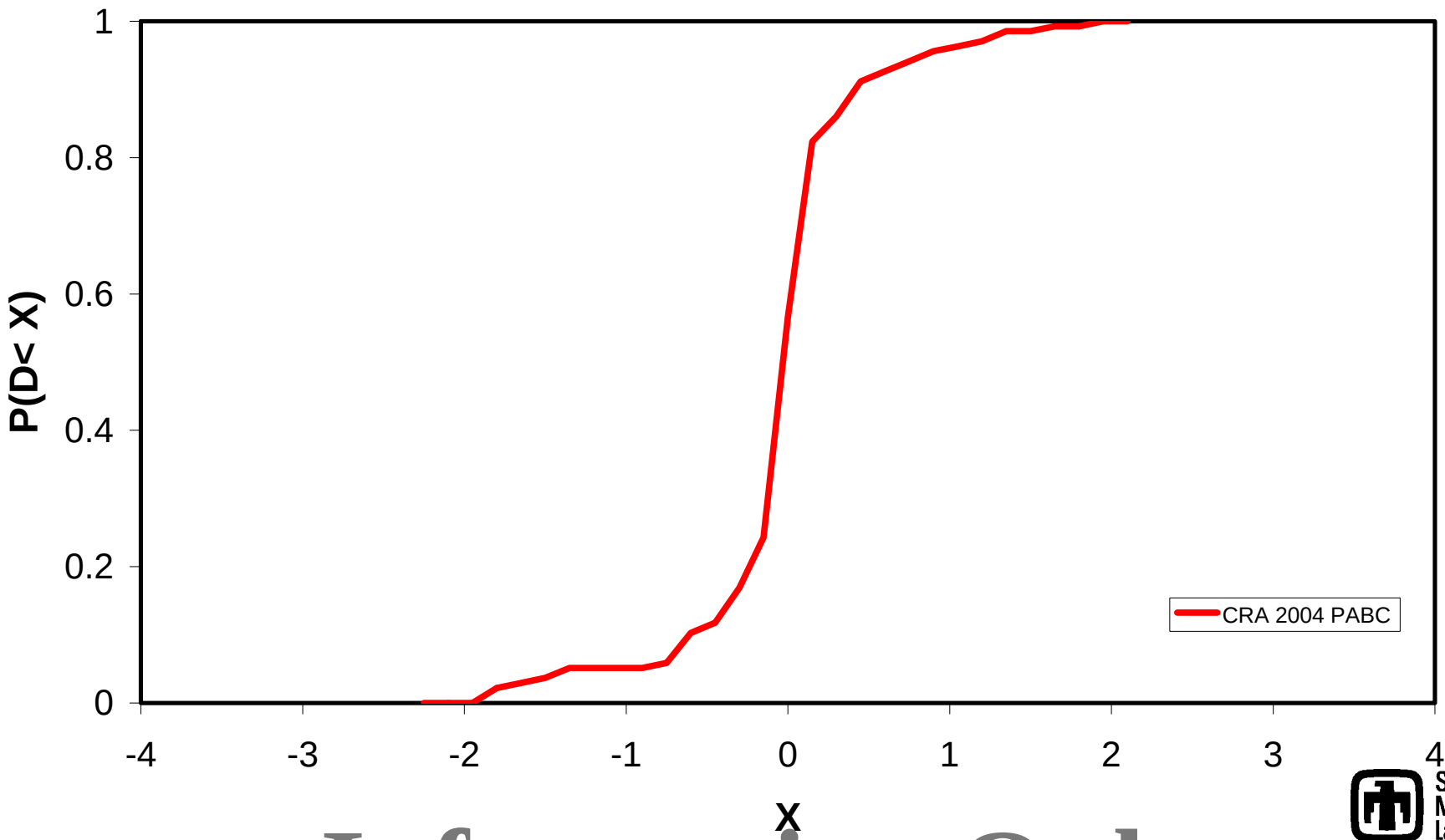
CUMULATIVE DISTRIBUTION FUNCTION FOR Np(V)



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CONCLUSIONS

- FMT code with Pitzer equations can predict actinide solubilities in brines with high ionic strength at 25 ^{o}C.
- FMT code is qualified for predicting actinide solubilities for the WIPP, and such predictions have been accepted by US EPA for the Compliance Certification Application (CCA) and Compliance Re-Certification Applications (CRA) for the WIPP.
- Uncertainty ranges and probability distribution of actinide solubilities for PA are established by comparing solubility values predicted by FMT with those independent experimental values in various solutions.

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Meeting Advertisement

- **Geological Society of America 2010 Annual Meeting, October 31- November 3, Denver, CO**
  - **T101. Near Field Geochemical Conditions of Geological Repositories for Nuclear Waste: New Experimental Work and Computer Modeling**

Mineralogical Society of America; GSA Mineralogy, Geochemistry, Petrology, and Volcanology Division

Yongliang Xiong, Larry Brush

- **Studies on chemical species present in waste packages and waste inventories are encouraged. Contributions related to interactions of chemical species in natural solutions with chemical species in waste packages and waste inventories are also encouraged.**

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